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(54) Preparation of 1,1,1,3-tetrafluoropropene(1234ze)

(57) Disclosed is a process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene (1234 ze) which comprises (a) contacting 1,1,1,3,3-pentafluoropropane (245fa) with an alkaline solution, preferably an aqueous or alcoholic solution of a base such as KOH, NaOH, Ca $(OH)_2$ or $Mg(OH)_2$, or with a chromium-based catalyst, such as fluorided Cr_2O_3 or fluorided Cr/Ni/AlF_3, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the reaction mixture.

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Description

[0001] This invention relates to preparation of cis/trans 1,1,1,3-tetrafluoropropene ("1234ze"), a monomer useful for the preparation of various homopolymers and copolymers, particularly to processes for the dehydrofluorination of 1,1,1,3,3-pentafluoropropane ("245fa"), a known blowing agent, to 1234ze using a chromium-based catalyst or a strong base. While the prior art, R. N. Haszeldine, J. Chem. Soc., 1952 (3490), describes the synthesis of cis/trans 1,1,1,3-tetrafluoropropene by fluorination of 1,1,1-trifluoro-2-propyne, this latter feed stock material is not available commercially.

[0002] Herein provided is a process for the preparation of 1234ze which comprises

(a) contacting 245fa with an alkaline solution or with a chromium-based catalyst, and

(b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0003] It has now been discovered that the cis and trans isomers of 1,1,1,3-tetrafluoro-2-propene (1234ze) can be conveniently prepared by dehydrofluorination of the blowing agent, 245fa, using either a strong base (either an aqueous or alcoholic solution) or a chromium-based catalyst.

[0004] The catalyzed process is preferably carried out in the gas phase. Use of an oxygen-containing gas such as air is desired to extend the catalyst lifetime, the level of oxygen generally being from about 1 to about 10 volume percent (preferably about 2 to 5%), based on the volume of the organic feed. Temperatures of from about 100°C. to about 600°C. are typically used, preferably from about 300°C. to about 400°C. The pressure can be atmospheric. Contact time (total flow rate per catalyst volume) is typically from about 1 to about 60 seconds, preferably from about 20 to 50 seconds. The catalyst is a chromium-based catalyst such as fluorided chromium oxide, Cr_2O_3, which chromium-based catalyst is either unsupported or supported on a support such as activated carbon, graphite, fluorided graphite or fluorided alumina, the chromium catalyst being used alone or in the presence of a co-catalyst selected from a nickel, cobalt, manganese or zinc salt. Two such preferred chromium catalysts are high surface area chromium oxide and chromiuminickel on fluorided alumina ($Cr/Ni/AlF_3$), preparation of this latter catalyst being taught, for example, in European Patent 486333. The chromium-based catalysts are preferably activated before use, typically by a procedure wherein the catalyst bed is heated to about 370°-380°C. (normally with a continuous flow of nitrogen), after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed for about 18 hours.

[0005] The dehydrofluorination can also be accomplished using an alkaline solution of a strong base, such as an aqueous or alcoholic solution of potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) or magnesium hydroxide ($Mg(OH)_2$). For the alcoholic solution, a conventional alcohol such as ethanol can be used. The solution typically is from about 0.01 to about 10 molar, preferably 0.1 to 5 molar. The dehydrofluorination is typically conducted at a temperature of from about 20°C. to about 100°C., preferably from about 20°C. to about 50°C.

[0006] The following examples are illustrative.

[0007] Example 1. 52.4 Grams of a high surface area Cr_2O_3 catalyst was activated by first feeding 30 ccm of nitrogen for 2 hours at 370°C. followed by cofeeding 30 ccm of HF and 30 ccm of nitrogen for 18 hours at 370°C. Subsequently, a mixture of 20 ccm of 245fa and 3 ccm of air (equal to about 3 volume % of oxygen, based on the 245fa volume) was fed over the catalyst bed at 400°C for a contact time of 45 seconds. Conversion was 96.2%. Selectivity for the desired (1234ze) product was about 96.3% (about 18.5% cis, about 77.8% trans). Performance of the catalyst was steady for 360 hours.

[0008] Example 2. Example 1 was repeated using $Cr/Ni/AlF_3$ catalyst (activated at 370°C. using a cofeed of 30 ccm of nitrogen and 30 ccm of HF for 18 hours) in a series of 3 tests, using the same temperature and air/245fa feed ratio, but with the contact time between 26 and 39 seconds. Conversions ranged from 88 to 94.5%. Selectivity for the desired (1234ze) product ranged from 96.2 to 98.5% (17.7 to 20.5% cis, 77 to 80.5% trans).

[0009] Example 3. 10 ccm of 245fa was bubbled through 3000 ml of 2.7 molar KOH solution at room temperature (about 20°C.). Analysis of the gaseous dry product, using gas chromatography on line, showed 26% conversion, with selectivity for the desired (1234ze) product of 97.9% (23.9% cis, 74% trans).

Claims

1. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an alkaline solution or with a chromium-based catalyst, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

2. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an aqueous or alcoholic solution of base selected from the group consisting of potassium hydroxide, sodium hydroxide, calcium hydroxide or magnesium hydroxide, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

3. A process as in Claim 2 wherein step (a) comprises contacting 1,1,1,3,3-pentafluoropropane with an aqueous potassium hydroxide solution.

4. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr_2O_3 or $Cr/Ni/AlF_3$, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

5. A process as in Claim 4 wherein the catalyst is fluorided Cr_2O_3.

6. A process as in Claim 4 wherein the catalyst is fluorided $Cr/Ni/AlF_3$.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 5781

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	KNUNYANTS I L ET AL: "REACTIONS OF FLUORO OLEFINS. COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS" BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OF CHEMICAL SCIENCES, 1 January 1960 (1960-01-01), pages 1312-1317, XP000578879 ISSN: 0568-5230 See p. 1313, reaction (XI) -> (XIII) and p. 1316, sixth paragraph. ---	1-3	C07C17/25
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	15 February 2000	Janus, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

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MUNICH	15 February 2000	Janus, S

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 30 5781

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82